Silicon diffusion in aluminum for rear passivated solar cells

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We show that the lateral spread of silicon in a screen-printed aluminum layer increases by \((1.50 \pm 0.06) \mu m/°C\), when increasing the peak firing temperature within an industrially applicable range. In this way, the maximum spread limit of diffused silicon in aluminum is predictable and does not depend on the contact area size but on the firing temperature. Therefore, the geometry of the rear side pattern can influence not only series resistance losses within the solar cell but the process of contact formation itself. In addition, too fast cooling lead to Kirkendall void formations instead of an eutectic layer. © 2011 American Institute of Physics. [doi:10.1063/1.3579541]

The improvement of solar cell efficiency in industrial production has motivated important contributions to rear surface passivation techniques. However, the optimization of the local contacts between screen-printed aluminum pastes and silicon is not trivial and requires deeper understanding of the metal– semiconductor interaction. Indeed, a compromise between the contact area and finger spacing is an essential issue when reducing series resistance. On the other hand, the local formation of a high-quality \(p^+\)-doped layer [back-surface-field (BSF)] to improve the cell performance, is still a challenge. Recently, it has been shown that the high overlapping of aluminum on each side of the local contact opening is essential for a well-formed local BSF and the minimization of the contact resistivity. Thereby, the design of the rear side pattern can influence the series resistance losses and the process of contact formation. In this letter, we search for the minimum contact spacing allowed for an optimal rear side pattern based on the interdiffusion between liquid aluminum and silicon. These results may have applications on screen-printed back-contacted and rear passivated silicon solar cells.

Figure 1(a) shows the cross-section of a silicon solar cell with a passivated and locally contacted rear side, as a model for this letter. Three variables describe the rear side structure—the width of the local contact openings (LCO), \(d_1\); the maximum spread limit of diffused silicon in aluminum layer, \(d_2\); and the contact spacing, \(L_p\). Thus, \((d_2-d_1)/2\) represents the spread of silicon in aluminum on each side of the LCO (away from the contact area). As shown in the cross-sectional model of Fig. 1(a), the contact area between silicon and aluminum is restricted to the LCO, \(d_1\). An aluminum layer fully covers the rear surface. The local BSF forms in the LCO at the rear of the device structure due to local aluminum-silicon interaction. The microscope image of Fig. 1(b) shows a section of the rear side of a processed solar cell with the same rear structure as shown by Fig. 1(a). The dark-gray regions (within \(d_1\)), which are visible after firing in the aluminum layer, do not represent the local BSF formation because they are wider than the LCO (\(d_2 > d_1\)). The understanding of this phenomenon motivated the development of the present study.

Polished Czochralski \(p\)-type silicon wafers with \((1.50 \pm 0.5) \Omega cm\) resistivity were fully covered with a dielectric insulation layer deposited by the plasma-enhanced chemical vapor deposition approach. The LCO (\(d_1\)) were achieved by screen printing an etching paste, which contains phosphoric acid, a useful etchant of dielectric films. The etching of the dielectric was performed by heating the wafers in an infrared belt furnace for 4 min at 330 °C. The dried etching paste was removed within a few seconds in an ultrasonic bath filled with 0.2% potassium hydroxide diluted with deionized water. A broad range of \(d_1\) was chosen between 100–500 \(\mu m\) in steps of 50 \(\mu m\) (the real values are \(\approx 20 \mu m\) broader due to the spreading of the etching paste). A state of the art 20 \(\mu m\) thick aluminum contact was screen-printed, fully covering the rear passivation layer and the opening lines. The alloy was formed after sintering the samples following a standard firing furnace profile. Three peak firing temperatures were applied: 750, 850, and 950 °C. The sharp limits of the visible dark-gray regions (\(d_2\)) were measured by optical microscopy.

The aluminum layer was characterized by scanning electron microscopy (SEM) and energy dispersive spectrometry/energy dispersive x-ray (EDS/EDX). The three layers (A, B, C), as shown by Fig. 1(a), are as follows: the local BSF (A, composition Si–1%Al); the eutectic layer or aluminum-silicon alloy formation (B, composition Al–12.6%Si); and the aluminum layer in porous state, C. For rear passivated solar cells, we redefine the aluminum layer in two regions: (1) the visible dark-gray region (within \(d_1\)) in hypereutectic alloy (composition >Al–12.6%Si) and (2) the rest of the aluminum layer formed by solid particles of the aluminum paste. Figure 2 shows on the y-axis the optical measurement of the dark-gray regions (spread limit of silicon in aluminum,
electron beam focused to 660 nm in diameter. Counts at the
edges of the interface in both lateral directions into the wide
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forms homogeneously below the contacts, up to 8 μm deep.

contrary to other authors,17 a homogeneous BSF forms below the void. The silicon composition in the aluminum layer, for the sample with a void, is shown by Fig. 3(d). It is described as an irregular form with a higher concentration at the center of the opening and two maxima located more than 150 μm away from the center of the opening, to the left and right. An explanation for this phenomenon is given by the following model of the local contact formation between aluminum and silicon.

The formation of the aluminum-silicon alloy begins with the melting of aluminum. The liquid aluminum wets the silicon surface in the local openings made in the dielectric, and then silicon dissolves in the aluminum layer. The depth of penetration of aluminum in silicon is a function of the temperature and of the aluminum spherical diameter.21 For a peak firing temperature of 950 °C, the depth of penetration is 20 μm, as shown by Figs. 3(a) and 3(c). Due to the higher solubility of silicon in aluminum than that of aluminum in silicon,16,20 a higher volume of silicon atoms diffuse in the aluminum than aluminum atoms in the silicon. If the peak firing temperature is too high, the diffusion is enhanced and silicon spreads deeper in the aluminum layer. At the interface, the aluminum in direct contact with the silicon bulk saturates first, then the silicon diffusion proceeds from the edges of the interface in both lateral directions into the wide amount of liquid aluminum mass, which is not yet saturated by silicon. After few seconds, a large amount of silicon atoms is found in the aluminum layer, more than 370 μm away from the contact area. The strong presence of aluminum atoms converts the immediately adjacent surface at the penetration, to p-type silicon (local BSF). Once the firing temperature has reached the maxima, the liquid solution saturates.

When the contact size is too broad, more silicon surface interacts with the aluminum particles, and the melt located in the middle part of the interface (LCO) will saturate too fast.

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ference (LCO), as already published elsewhere15,16 [see Fig. 3(b)].

Figure 3(a) shows an eutectic layer formed below the aluminum layer for a \(d_1 = 50 \) μm. Its silicon concentration, as shown by Fig. 3(b), follows a Gaussian fit centered at the LCO, decreasing to the left and right, to the predicted spread limit of 375 μm. From the Gaussian fit, the maximum concentration is represented by 27 counts, while the concentration at the spread limit \((d_2 - d_1)/2\) is represented approximately by three counts. For a high peak firing temperature of 950 °C a silicon concentration of \(C[(d_2 - d_1)/2]/C_{0} = 11.11\%\) is still present in the aluminum layer at the spread limit of silicon, 375 μm far away from the LCO. The BSF forms homogeneously below the contacts, up to 8 μm deep.

Figure 3(c) shows no eutectic layer formed below the contacts but shows instead a void. For this sample, the aluminum was deposited on a broader contact opening \((d_1 = 125 \) μm) and fired at the high peak firing temperature (fast cooling). The void present is normally found in samples with broader LCO and which are cooled too fast. Contrary to other authors,17 a homogeneous BSF forms below the void. The silicon composition in the aluminum layer, for the sample with a void, is shown by Fig. 3(d). It is described as an irregular form with a higher concentration at the center of the opening and two maxima located more than 150 μm away from the center of the opening, to the left and right. An explanation for this phenomenon is given by the following model of the local contact formation between aluminum and silicon.

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When the contact size is too broad, more silicon surface interacts with the aluminum particles, and the melt located in the middle part of the interface (LCO) will saturate too fast.
Furthermore, below too high firing temperatures (fast cooling), a high elastic stress field may occur in the melt during the alloying. Due to the Kirkendall effect, which explains that the rates at which two types of atoms diffuse are not the same, the high generation of vacancies during the silicon-aluminum interdiffusion may coalesce in the melt, causing the nucleation and formation of Kirkendall voids instead of an eutectic layer.

By cooling down the sample, the composition of silicon in the liquid-phase has to decrease following the liquid curve of the binary system, however, only the edges of the LCO are still in direct contact with the aluminum layer due to the presence of the void. By reaching the eutectic temperature, no more silicon segregates and the whole remaining liquid solidifies, leaving a high concentration of silicon in aluminum, away from the surface of contact [shown by the two maxima of Fig. 3(d)]. If the interaction between aluminum and silicon takes place only within \( d_2 \), where a visible dark-gray region is sharply delimited, the spread of silicon in the aluminum layer is diffusion-limited. Thereby, an exponential decrease with the distance from the center of the interface is evident due to the Fick’s law of diffusion.

Because the diffusion of silicon in the liquid aluminum proceeds laterally within the aluminum layer, a large amount of aluminum should overlap each side of the dielectric opening to achieve an optimal metal–semiconductor interaction. This overlapping of aluminum on narrow dielectric openings is evident due to the reduction in the contact resistivity and the homogeneous formation of the local BSF. We suggest that the maximum spread limit of diffused silicon, \( d_2 \), may determine the minimum width of the aluminum metallization needed for an optimal contact and full local BSF formation. Thus, the aluminum overlapping is determined by \( d_2 \). In this way, the finger spacing may also be determined by the spread limit of silicon in the screen-printed aluminum layer (\( L_p \geq d_2 \)). Another application of the aluminum overlapping may be found on interdigitated back-contact n-type silicon solar cells to obtain high-quality screen-printed aluminum-alloyed emitters.

In conclusion, we give further understanding of the local contact formation between a screen-printed aluminum paste and narrow silicon contact areas. The spread of silicon in a screen printed aluminum layer increases by \( 1.5 \pm 0.06 \) \( \mu m/\degree C \) when increasing the peak firing temperature in a range of 750–950 \( \degree C \). This lateral spread limit of silicon, on each side of the dielectric opening, does not depend on the contact area size but on the firing temperature, and is predicted as 75 \( \mu m \), 225 \( \mu m \), and 375 \( \mu m \) for 750 °C, 850 °C, and 950 °C, respectively. Thus, the width of the aluminum contact may be determined by the maximum spread limit of diffused silicon in an aluminum layer. We suggest that the contact spacing should be equal or larger than the maximum spread limit of diffused silicon in aluminum. Additionally, the void formation below the aluminum-silicon contacts may be explained by the Kirkendall effect. Our result may be applied to develop high-efficiency screen-printed back-contacted and rear passivated solar cells suitable for industry.

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